Effect of ice-quenching on the change in hardness of a Pd-Au-Zn alloy during porcelain firing simulation

Hye-Jeong SHIN, Min-Jung KIM, Hyung-II KIM, Yong Hoon KWON and Hyo-Joung SEOL

Department of Dental Materials, Institute of Translational Dental Science and BK21 PLUS Project, School of Dentistry, Pusan National University, Beomeo-Ri, Mulgeum-Eup, Yangsan-Si, Gyeongsangnam-Do, 626-814, South Korea
Corresponding author, Hye-Joung SEOL; E-mail: seol222@pusan.ac.kr

This study examined the effect of ice-quenching after degassing on the change in hardness of a Pd-Au-Zn alloy during porcelain firing simulations. By ice-quenching after degassing, the specimens were softened due to homogenization without the need for an additional softening heat treatment. The lowered hardness by ice-quenching after degassing was recovered greatly from the first stage of porcelain firing process by controlling the cooling rate. The increase in hardness during cooling after porcelain firing was attributed to the precipitation of the f.c.t. PdZn phase containing Au, which caused severe lattice strain in the interphase boundary between the precipitates and matrix of the f.c.c. structure. The final hardness was slightly higher in the ice-quenched specimen than in the specimen cooled at stage 0 (the most effective cooling rate for alloy hardening) after degassing. This was attributed to the more active grain interior precipitation during cooling in the ice-quenched specimen after degassing.

Keywords: Pd-Au-Zn alloy, Porcelain firing simulation, Hardening mechanism, Cooling rate control, Ice-quenching

INTRODUCTION

Recently, the dental esthetic needs of patients have increased with economic development, which has prompted more research into esthetic dental prostheses. Porcelain, as an esthetic dental material, has a very low fracture resistance and insufficient strength to be used as an all-ceramic restoration itself. Therefore, methods to improve the mechanical properties and reduce the fracture under stress have been devised. The most well-known strengthening method is to use a metal substructure under a ceramic superstructure.

The metal substructure needs to undergo a suitable adjustment, such as trimming for adaptation on the master model after casting. Subsequently, degassing, which is the first step in the firing process for bonding porcelain, is performed at the highest temperature. Therefore, sag and thermal distortion of the metal substructure can occur easily. If this occurs, the metal substructure needs to be readjusted after degassing.

The degassing treatment is generally conducted at approximately 1,000°C, where the alloy might be softened. Therefore, by ice-quenching after degassing, the alloy may remain soft without a softening heat treatment. For the efficiency of the adjustment, it is advantageous that an adjustment be made for an alloy that is not too hard to trim. Therefore, if a readjustment is performed for an ice-quenched metal substructure after degassing, it will improve the efficiency of the adjustment. If such ice-quenching can be applied after degassing, the alloy softened by ice-quenching must recover its hardness during the remaining firing process to achieve the appropriate mechanical properties of the final prosthesis. To verify this, a Pd-Au-Zn alloy, which is one of the representative dental alloys for metal-ceramic crowns, was used in the present study. A previous study with a 50.37Pd-30.61Au-9.92In-6.09Ag (at%) alloy with minor ingredients reported that pre-softening heat-treatment of the alloy induced precipitation more actively during the porcelain firing process, resulting in apparent hardening. Similarly, in the present study, the alloy softened by ice-quenching was expected to recover its hardness during the remaining firing process for bonding porcelain. To verify this, this study examined the effect of ice-quenching after degassing on the change in hardness of a Pd-Au-Zn alloy during porcelain firing simulation by analyzing the changes in hardness, microstructure, phase transformation, and elemental distribution.

MATERIALS AND METHODS

Specimen alloy

The specimen alloy used in this study was a Pd-Au-Zn-based high gold-content alloy without silver for bonding porcelain (Surefire 10, Aurium Research, San Diego, CA, USA); it had a white color and fine grains. The manufacturer reported the alloy to have a melting range of 1,160–1,250°C and a casting temperature of 1,350°C. Table 1 lists the chemical composition of the specimen alloy supplied by the manufacturer.

The specimens were cast using the lost wax casting technique in a standard broken arm centrifugal casting machine (Centrifugal casting machine, Osung, Gimpo, Korea), and then melted using a multi-orifice gas-oxygen torch. All castings were bench cooled to room temperature. After divesting, the specimens were cleaned using an ultrasonic cleaner (Bransonic, Color figures can be viewed in the online issue, which is available at J-STAGE.

Received Aug 9, 2016: Accepted Sep 20, 2016
Table 1  Chemical composition of the specimen alloy

<table>
<thead>
<tr>
<th>Composition</th>
<th>Pd</th>
<th>Au</th>
<th>Zn</th>
<th>In</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>37.5</td>
<td>51.5</td>
<td>6.0</td>
<td>2.4</td>
<td>2.4</td>
</tr>
<tr>
<td>at%</td>
<td>47.19</td>
<td>35.01</td>
<td>12.29</td>
<td>2.8</td>
<td>2.71</td>
</tr>
</tbody>
</table>

Table 2  Simulated porcelain firing cycles

<table>
<thead>
<tr>
<th>Firing cycles</th>
<th>Pre-drying (min)</th>
<th>Heat rate (°C/min)</th>
<th>Start temp. (°C)</th>
<th>Final temp. (°C)</th>
<th>Hold time (min)</th>
<th>Vacuum time (min)</th>
<th>Vacuum level (hpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degassing</td>
<td>0</td>
<td>70</td>
<td>600</td>
<td>1,010</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Wash</td>
<td>2</td>
<td>70</td>
<td>600</td>
<td>950</td>
<td>1</td>
<td>6:00</td>
<td>50</td>
</tr>
<tr>
<td>Opaque</td>
<td>2</td>
<td>70</td>
<td>600</td>
<td>930</td>
<td>1</td>
<td>5:43</td>
<td>50</td>
</tr>
<tr>
<td>Main bake</td>
<td>4</td>
<td>70</td>
<td>600</td>
<td>920</td>
<td>1</td>
<td>5:34</td>
<td>50</td>
</tr>
<tr>
<td>Correction</td>
<td>4</td>
<td>70</td>
<td>600</td>
<td>910</td>
<td>1</td>
<td>5:26</td>
<td>50</td>
</tr>
<tr>
<td>Glaze</td>
<td>0</td>
<td>70</td>
<td>600</td>
<td>900</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 3  Cooling rate during the simulated porcelain firing cycles

<table>
<thead>
<tr>
<th>Cooling rate</th>
<th>Stage 0</th>
<th>Stage 1</th>
<th>Stage 2</th>
<th>Stage 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condition</td>
<td>Firing chamber moves immediately to the upper end position</td>
<td>Firing chamber opens about 70 mm</td>
<td>Firing chamber opens about 50 mm</td>
<td>Firing chamber remains closed</td>
</tr>
</tbody>
</table>

Branson, St. Louis, MO, USA) for 30 min. The specimens obtained were in the form of small square pieces, 10×10×0.8 mm in size.

Porcelain firing simulation
The as-cast specimens underwent a degassing treatment in a dental porcelain furnace (Multimat 2 Touch, Dentsply, Konstanz, Germany) according to the porcelain firing process listed in Table 2. To determine the most effective cooling rate for alloy hardening, various cooling rates were attempted after degassing, as listed in Table 3. For the specimens which were degassing treated and then ice-quenched or cooled at the most effective cooling rate for hardening, the remaining porcelain firing process was simulated in a porcelain furnace. At this time, the cooling rate was fixed to the most effective cooling rate for hardening.

Hardness test
The changes in hardness during porcelain firing simulation were examined using a Vickers microhardness tester (MVK-H1, Akashi, Tokyo, Japan) with a 300 gf load and a dwell time of 10 s. The hardness values recorded were the mean of five measurements for each specimen.

Field emission scanning electron microscopy (FE-SEM) observations
The microstructural changes during the porcelain firing simulation were examined by FE-SEM (JSM-6700F, JEOL, Tokyo, Japan) at an accelerating voltage of 15 kV. The specimens were polished metallographically and etched in an aqueous solution containing 10% KCN (potassium cyanide) and 10% (NH₄)₂S₂O₈ (ammonium persulfate). Subsequently, the surfaces of the specimens were observed by FE-SEM.

X-ray diffraction (XRD)
XRD (XPERT-PRO, Philips, Almelo, Netherlands) was performed to examine the phase transformation during the porcelain firing simulation. The XRD profile was recorded at 30 kV and 40 mA using Ni-filtered Cu Kα radiation as the incident beam. The scanning rate of the goniometer was 1° (2θ)/min.

Energy dispersive spectrometry (EDS)
The ice-quenched specimens after degassing underwent simulated porcelain firing. They were then polished metallographically and etched in an aqueous solution, as done for the FE-SEM observations. The elemental distribution was analyzed using an energy dispersive X-ray spectrometer (INCA x-sight, Oxford Instruments Abingdon, UK).
RESULTS

Change in hardness according to the cooling rate after degassing

The hardness of the as-cast specimen was 253.2 (±6.01) HV (Fig. 1). By ice-quenching after degassing, the hardness of the specimen was reduced by 58.7 HV compared to that in the as-cast state. The highest hardness, 267 (±3.06) HV, was obtained in the specimen cooled at the cooling rate of stage 0. The hardness decreased with decreasing cooling rate but the decrease in hardness was stopped since stage 2. Therefore, there is a most effective cooling rate for hardening of the alloy during cooling after firing for bonding porcelain.

Effect of ice-quenching after degassing on the change in hardness during porcelain firing simulation

To observe the effect of ice-quenching after degassing on the change in hardness during porcelain firing simulation, the degassing-treated specimens were cooled at two different cooling rates, ice-quenching and stage 0 (the most effective cooling rate for alloy hardening). They were firing simulated according to the firing process listed in Table 2. At this time, the cooling rate was fixed to stage 0 for each specimen. In the specimen cooled at stage 0 after degassing, the change in hardness barely appeared during the firing process (Fig. 2). In the specimen softened by ice-quenching after degassing, the hardness was recovered mostly from the first stage of the remaining firing process, the wash stage. The final hardness of the ice-quenched specimen was slightly higher than that of the specimen cooled at stage 0 after degassing.

Effect of ice-quenching after degassing on the microstructural changes during porcelain firing simulation

In the as-cast specimen (Fig. 3a), an equiaxed structure was observed. The precipitates were observed in and adjacent to the grain boundaries. In the grain interior region, in addition to the particle-like precipitates, finer dot-like precipitates were observed, as shown at the circle in (a-3). In the ice-quenched specimen after degassing (Fig. 3b), the grain boundary precipitates disappeared, and particle-like precipitates in the grain interior transformed to smaller and uniform-sized precipitates. The finer dot-like precipitates almost disappeared in the matrix, as in the circle in (b-3). Therefore, a large amount of precipitates in the grain boundary and interior were dissolved in the matrix during the degassing process. In the specimen cooled at stage 0 after degassing (Fig. 3c), the grain boundary precipitates had regenerated partially, and particle-like precipitates became coarser compared to the specimen (b) that was ice-quenched after degassing. In the matrix, the finer dot-like precipitates regenerates, as observed in the circle in (c-3). In the complete firing simulated specimens after ice-quenching or cooling at stage 0 (Fig. 3d, e), the quantity of grain boundary precipitates increased significantly, and the particle-like precipitates in the grain interior became much coarser. The finer dot-like precipitates in the matrix were generated more actively in specimen (d) than (e), as shown in the circle in (d-3) and (e-3).

Effect of ice-quenching after degassing on the phase transformation during porcelain firing simulation

In the as-cast specimen (Fig. 4a), a face-centered cubic (f.c.c.) phase with a lattice parameter of $a_{1c}=3.96$ Å ($\alpha_1$ phase), and a face-centered tetragonal (f.c.t.) phase with lattice parameters of $a_{2c}=4.14$ Å, $c_{2c}=3.59$ Å ($\beta_1$ phase) were observed. Considering the diffraction peak intensity, the matrix was comprised of the $\alpha_1$ phase,
showing higher diffraction peak intensity, and the precipitates in the grain boundary and interior were comprised of the $\beta_1$ phase. In the ice-quenched specimen after degassing (Fig. 4b), the XRD peak intensity of the $\beta_1$ phase became very weak, as observed in the circle in Fig. 4b. On the other hand, in the specimen cooled at stage 0 after degassing (Fig. 4c), the peak intensity of the $\beta_1$ phase increased again. Accordingly, the precipitates newly appeared in the grain boundary and interior shown in the FE-SEM image of the corresponding specimen (Fig. 3c) were composed of the $\beta_1$ phase. In the complete firing simulated specimens (Fig. 4d, e), the intensity of the $\beta_1$ XRD peak increased more without any change in the peak position.

EDS was performed on the complete firing-simulated specimen after degassing and subsequent ice-quenching (Fig. 5). Table 4 lists the results of EDS point analysis for each region marked with the arrow.
Table 4  EDS analysis after complete firing simulation of the ice-quenched specimen after degassing

<table>
<thead>
<tr>
<th>Region (at%)</th>
<th>Pd</th>
<th>Au</th>
<th>Zn</th>
<th>In</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix</td>
<td>1</td>
<td>46.03</td>
<td>34.87</td>
<td>12.23</td>
<td>3.67</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>45.63</td>
<td>32.97</td>
<td>14.16</td>
<td>3.82</td>
</tr>
<tr>
<td>Precipitate</td>
<td>1</td>
<td>49.92</td>
<td>29.43</td>
<td>16.09</td>
<td>2.22</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>49.57</td>
<td>29.29</td>
<td>16.43</td>
<td>2.39</td>
</tr>
</tbody>
</table>

Fig. 5  Microstructure after complete firing simulation of the ice-quenched specimen after degassing (M: matrix, P: precipitates).

in Fig. 5 (M: matrix, P: precipitates). In the matrix region (M), the elemental distribution was similar to the chemical composition of the as-received alloy (Table 1). In the grain boundary precipitates (P), the concentration of Pd and Zn was higher and that of Au lower than that in the matrix.

**DISCUSSION**

Porcelain, as an esthetic dental material, has very low fracture resistance characteristics and insufficient strength to be used as an all-ceramic restoration itself\(^1\). Recently, techniques for improving the mechanical properties and reducing the fracture of porcelain have been devised, and the most well-known strengthening method is to use a metal substructure under a ceramic superstructure\(^2\). The metal substructure needs to undergo an appropriate adjustment, such as trimming for adaptation to the master model after casting. Subsequently, degassing is performed at approximately 1,000°C, where sag and thermal distortion of the metal substructure can take place easily\(^4\). If this occurs, the metal substructure needs to be readjusted after degassing. For the efficiency of the adjustment, it is helpful that the adjustment be made for an alloy that is not too hard to trim. In this study, by ice-quenching the specimen alloy after degassing, it was revealed that the degassing treatment itself makes the alloy soft, but the cooling process after degassing makes the alloy hard (Fig. 1)\(^8\). Therefore, if readjustment is performed for a softened alloy by ice-quenching after degassing, it will improve the efficiency of the adjustment. By proper cooling after each remaining firing process, the softened alloy by ice-quenching can then recover its hardness to achieve the appropriate mechanical properties of the final prosthesis.

To determine if the alloy softened by ice-quenching
after degassing recovers its hardness efficiently by proper cooling after each remaining firing process, the hardness changes during firing simulation were observed. First of all, to obtain the most effective cooling rate for hardening of the alloy, various cooling rates (Table 3) were tried after degassing. As a result, the most effective cooling rate was stage 0 (Fig. 1), which is a relatively fast cooling rate. Such an effective cooling rate for alloy hardening was reported to vary according to the composition of the alloys\(^7,10-12\). From the apparent hardening during cooling, the alloy was believed to have undergone precipitation or atomic ordering during cooling.

To determine if the ice-quenched specimen after degassing recovers its hardness during the remaining firing process, the change in hardness during the porcelain firing simulation was compared with that of the specimen cooled at stage 0 after degassing. The cooling rate during the remaining firing process (Table 2) was fixed to stage 0 for each specimen. As a result, in the specimen cooled at stage 0 after degassing, the change in hardness barely appeared during the remaining firing process. This is unlike the hardness changes in the Pd-Ag-Sn alloy, which showed apparent softening during the porcelain firing process\(^7\). On the other hand, the ice-quenched specimen after degassing recovered its hardness mostly from the first stage of the remaining firing process, the wash stage (Fig. 2). Such rapid recovery in the hardness according to the cooling rate control during the porcelain firing process was also reported for Pd-Au-In-Ag and Pd-Ag-Au-Sn alloys, which had undergone a pre-softening heat treatment before porcelain firing\(^7,10\). From the above, if the readjustment is done for the ice-quenched metal substructure after degassing, it will increase the efficiency of processing without affecting the mechanical properties of the final prosthesis.

The microstructural changes showed that the softening of the ice-quenched specimen after degassing resulted from microstructural homogenization (Fig. 3). This corresponded to the XRD results, which showed that the XRD peak intensity of the precipitates became very weak in the ice-quenched specimen (Fig. 4). By cooling the ice-quenched specimen at stage 0 after the remaining firing process, the precipitates dissolved in the matrix re-precipitated from the grain boundary and interior (Fig. 3), resulting in apparent hardening\(^7,11,13,14\). Finally, in the ice-quenched specimen after degassing, the quantity of grain boundary precipitates increased significantly, and the particle-like precipitates in the grain interior became coarse by the complete firing simulation, showing a similar microstructure to that of the specimen cooled at stage 0 after all the firing process. The finer dot-like precipitates in the matrix were generated more actively in the ice-quenched specimen after degassing (Fig. 3), as it was in the pre-softening heat treated Pd-Au-In-Ag alloy\(^7\). Therefore, the final hardness after the complete firing simulation was slightly higher in the ice-quenched specimen than in the specimen cooled at stage 0 after degassing (Fig. 2).

From the XRD study (Fig. 4), the precipitation hardening was related to the formation of the \(\beta_1\) phase with an f.c.t. structure, which forms severe lattice strain in the interphase boundary between the \(\beta_1\) precipitates and the surrounding \(\alpha_1\) matrix of the f.c.c. structure\(^7,10,11,12\). By considering the EDS results (Fig. 5) together with the XRD results, the \(\alpha_1\) matrix was composed of the Pd-Au-rich phase, and the \(\beta_1\) precipitates were composed of the AuCu-type PdZn phase containing relatively large amounts of Au\(^17,18\). The obtained lattice parameters of the AuCu-type PdZn phase were \(a_{200}=4.14\) Å and \(c_{111}=3.59\) Å in the present study, which showed larger \(c\) value than the reported value (\(a=4.1\) Å, \(c=3.295\) Å)\(^{19}\). Considering the fact that Au has larger atomic size than Zn\(^19\), the difference in the \(c\) value was thought to be resulted from the relatively high Au content in the alternating \(\text{Zn}\) layer which is formed along the c-axis of the PdZn phase.

**CONCLUSION**

These results showed that by ice-quenching after degassing, the specimens softened due to homogenization without an additional softening heat treatment. The hardness lowered by ice-quenching after degassing was recovered greatly from the first stage of the remaining porcelain firing process by controlling the cooling rate. The increase in hardness during cooling after the porcelain firing process resulted from the precipitation of the f.c.t. PdZn phase containing Au from the surrounding matrix of the f.c.c. structure. The final hardness after complete porcelain firing was slightly higher in the homogenized specimen by ice-quenching than in the specimen cooled at stage 0 (most effective cooling rate for alloy hardening) after degassing due to more active grain interior precipitation.

**ACKNOWLEDGMENTS**

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (grant number: NRF-2014R1A1A2055018)

**REFERENCES**

6. Prakash P, D’Souza D, Kumar M, Viswambaran M. Effect of firing cycle and surface finishing on the sag resistance of long-


